

DIRECT QUANTIFICATION OF THORIUM, URANIUM AND RARE EARTH ELEMENT CONCENTRATIONS IN NATURAL WATERS BY ICP-MS

Helena E. L. Palmieri¹, Eliana A. N. Knupp¹, Lúcia M. L. A. Auler¹, Luiza M. F. Gomes², Claudia C. Windmüller²

¹ Centro de Desenvolvimento da Tecnologia Nuclear (CDTN/CNEN)
Av. Presidente Antônio Carlos, 6627
CAMPUS da UFMG – Pampulha
31270-901 – Belo Horizonte - MG
help@cdtn.br

² Universidade Federal de Minas Gerais (UFMG)/Departamento de Química,
Av. Antonio Carlos 662731270-901 – Belo Horizonte – MG

ABSTRACT

A direct quantification of the thorium, uranium and rare earth elements in natural water samples using inductively coupled plasma mass spectrometry (ICP-MS) was evaluated with respect to selection of isotopes, detection limits, accuracy, precision, matrix effects for each isotope and spectral interferences. Accuracy of the method was evaluated by analysis of Spectra pure Standards (SPS-SW1 Batch 116-Norway) for the rare earth elements (REEs), thorium, uranium, scandium and yttrium. The measurements were carried out for each of the following analytical isotopes: ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴³Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁶⁰Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁷Er, ¹⁶⁹Tm, ¹⁷⁴Yb, ¹⁷⁵Lu, ⁴⁵Sc, ⁸⁹Y, ²³²Th and ²³⁸U. Recovery percentage values found in these certified samples varied between 95 and 107%. The method was applied to the analysis of spring water samples collected in fountains spread throughout the historical towns of Ouro Preto, Mariana, Sabará and Diamantina in the state of Minas Gerais, Brazil. In the past these fountains played an essential and strategic role in supplying these towns with potable water. Until today this water is used by both the local population and tourists who believe in its quality. REE were quantified at levels comparable to those found in estuarine waters, which are characterized by low REE concentrations. In two fountains analyzed the concentration of REEs presented high levels and thus possible health risks for humans may not be excluded.

1. INTRODUCTION

The rare earth elements, REEs or "rare earths", also known as the lanthanide series of elements represents a group of 15 elements from La to Lu, which possesses similar chemical and physical properties and forms a geochemical coherent group. Among them, Promethium (Pm) does not occur naturally in the Earth's crust. They play an important role in various fields ranging from geology to electronics, which demand their determination from percentage to ultra-trace level [1]. The importance of the determination of REEs, yttrium (Y), thorium (Th) and uranium (U) in drinking water is related to possible adverse health effects caused by these elements.

Increasing use of rare earth elements for different applications increases their release into the environment where REE traces are bio-accumulated by organisms. Their bioavailability and toxic properties are currently under investigation and REE are known to activate or inhibit metabolism or enzyme activity [2]. As a consequence, REEs are already part of national and EU legislation [3]. Hence, the development of sensitive, precise and accurate analytical

methods for their determination in various environmental matrices including water is necessary.

REE concentrations in waters are typically in the ng/L range, except for some geothermal and acid waters that have REE concentrations in the $\mu\text{g/L}$ range. Prior to the advent of ICP-MS, REE concentrations in water were determined using neutron activation analysis (NAA) and isotope-dilution thermal ionization mass spectrometry (ID-TIMS). The first reported study of rare earth element concentrations in water was the analysis of seawater using NAA [4]. Using this method preconcentration of REEs and separation from elements that cause interferences are required. Analysis of REEs by ID-TIMS requires not only preconcentration and separation of the REEs, but also the addition of an enriched isotope to each element to be determined. However this method continues to be the most precise technique for REE determinations [5].

The introduction of inductively coupled plasma mass spectrometry in the 1980s brought a remarkable change in REEs analysis because of its very low detection levels, high sensitivity, large dynamic range, limited interference effects and simplified sample preparation procedures [3]. With no preconcentration or separation, detection limits for the REEs were 0.01-0.02 $\mu\text{g/L}$ with an analytical uncertainty of approximately 5% [6].

However ICP-MS analysis of REEs is known to be hampered by unwanted spectral and non spectral interferences [3]. Isobaric interferences, polyatomic ions and to a small extent (for Sc and Y) multiple charged ions are the most important spectral interferences, which are overcome usually by mathematical correction procedures. Non-spectral interferences can be divided in reversible, which can occur while the sample is being measured, and irreversible matrix effects: clogging of the nebulizer and sampling orifices or deposition on the torch or in the ion lens stack. The errors associated with non-spectral interferences can be eliminated by appropriate calibration procedures, adapted sample preparation or limitation of the amount of sample delivered to the nebulizer, plasma and sampling devices, for example by the application of flow injection [7].

The mass spectra are also plagued by other spectroscopic interferences, e.g. oxides and hydroxides, which pose serious problem for the determination of middle and heavier rare earth elements by ICP-QMS, particularly when the concentration ratio of lighter to heavier rare earths is high. In addition, Ba is one of the most abundant elements in many samples and its oxides and hydroxides also interfere with the determination of some of the rare earth elements, e.g. Eu [1].

The average of uranium in the earth's crust corresponds to 2 μg uranium per g of soil, being concentrated mainly in the acidic magmatic rocks with lesser amounts in basic minerals and sediments [8]. Soluble U (VI) carbonate complexes produced in soil uranium can be transferred into natural water. High values of uranium in drinking water and foodstuffs may lead to harmful effects in human beings.

Uranium has both chemical and radiological toxicity with the two important target organs being the kidney and lung [9, 10]. Concentrations of uranium as low as 500 $\mu\text{g/L}$ can affect the reproductive capability of aquatic organisms and its toxicity in fish was evidenced [11]. Therefore the determination of uranium in drinking and natural water is also of great importance. Various methods have been used for its determination in environmental and

water samples [8]; ICP-MS is an alternative technique for the determination of U and Th at ng/L trace levels, requiring a small sample volume, providing a fast analysis free from spectral interferences.

In this work, a direct quantification of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y, Th and U in natural water samples using the latest generation ICP-MS was evaluated with respect to selection of isotopes, detection limits, accuracy, precision, matrix effects, linear calibration range for each isotope and spectral interferences.

2. EXPERIMENTAL

2.1. Instrumentation and Reagents

All measurements were made using a Perkin Elmer ELAN DRC-e ICP-MS spectrometer equipped with auto sampler (AS-93plus), sea spray nebulizer, cyclonic spray chamber and a quadrupole analyzer consisting of 4 cylindrical bars of 20 cm length and 1 cm diameter, allowing mass spanning in the $1 < m/z < 240$ range in less than 0.1 s. Standard and sample solutions were aspirated into the argon plasma via a peristaltic pump and data were acquired using a Dell computer with a PerkinElmerSCIEX quantitative ELAN Version 3.4 software. The internal standard rhodium was added on-line to standards and samples from a bottle containing a solution of 20 µg/L Rh (Fluka, 8372) in 2% (v/v) nitric acid using a separate feeding tube on the peristaltic pump (Trident Internal Standard Kit- PerkinElmer).

A multi-element standard solution (Smart Tune solution-N8125040-Perkin Elmer) was used for daily performance evaluation and for lens calibration. Solutions, standards, and dilutions were prepared with ultra-pure water (18.2 MΩ.cm) obtained from a Milli Q Element System (Millipore, Belford, MA, USA). Ultrapure HNO₃ 69.5% (w/w) (Fluka) was used for the preparation of all standard solutions and in the preservation and dilution of the samples. Argon gas 99.999% purity, supplied by White Martins, was used for plasma, sample nebulisation, and as auxiliary gas.

REEs, Th, Y stock solution of 10.0 mg/L (Multi-element Standard 2 PerkinElmer N9300232) and U stock solution of 10.0 mg/L (Multi-element Standard 3 PerkinElmer N9301720) were used for preparing the calibration curve. All the solutions and samples were prepared in 1% HNO₃ for ICP-MS analysis and a surface water reference material (LGC-SPS-SW1) was used to evaluate the accuracy of the quantitative ICP-MS measurements.

2.2 ICP-MS Analytical Methodology

Before starting the analytical measurements, the plasma instrument was allowed to equilibrate for 30 min and then the daily performance check of the ICP-MS ELAN DRC-e is evaluated using a Smart Tune solution (10 µg/L Ba, Be, Ce, Co, In, Mg, Pb, Rh, U in 1% HNO₃). During the daily performance the instrument settings are optimized for sensitivity, interferences (oxides, double charged), background and precision. Sensitivity is checked through the intensities (cps) of ²⁴Mg (> 50 000), ¹¹⁵In (> 250 000) and ²³⁸U (> 200 000) and precision (< 2%) through the relative standard deviation (RSD) of these measurements. Oxides of Ce, mass 156 (corresponding to ¹⁴⁰Ce ¹⁶O⁺) and double charged of Ba mass 69

(corresponding to $^{138}\text{Ba}^{2+}$) should be below 3%. The background for mass 220 is typically below 25 and the RSD should be below 5.

Standards and samples were aspirated into the ICP-MS with 1 mL/min carrier flow and the isotopes selected were measured using the experimental conditions indicated in Table 1. Measurement data obtained were interpolated in a calibration curve of aqueous standards covering a concentration range from 0.05 to 2.0 $\mu\text{g/L}$ prepared with the same reagents as the samples. The instrumental detection limits (IDLs) and the method detection limits (MDLs) for the determination of the dissolved selected analytes in waters were determined according to U.S. EPA Method 200.8 for the Analysis of Drinking Waters [12].

Table 1. Operating conditions and ICP-MS settings for the determination of REEs, Sc, Y, Th and U

ICP-MS operating conditions		Mass spectrometer acquisition settings	
RF power	1200 W	Dwell time	50 ms
Nebulizer gas flow rate	0.72 L/min	Points per peak	1
Auxiliary gas flow rate	1.10 L/min	Sweeps per reading	20
Plasma gas flow rate	16 L/min	Readings per replicate	1
Lens setting	AutoLens	Replicates	3
Interface cones	Nickel	Scan mode	Peak hopping
Analog stage voltage	-1700 V	Detector mode	dual
Pulse stage voltage	1200 V		

3. RESULTS AND DISCUSSION

The selection of isotopes for determination of rare earth elements by ICP-MS was performed in agreement with Rault et al. [1] and Longerich et al. [13]. According to them, the following isotopes were selected for the measurements in the quantitative mode (abundances of the different isotopes in parenthesis): ^{89}Y (100%), ^{139}La (99.91%), ^{140}Ce (88.48%), ^{143}Nd (12.18%), ^{147}Sm (15.0%), ^{151}Eu (47.8%). In principle the isotope with the highest abundance is selected, provided that is free of isobaric or oxide interference. This is the case of the isotopes shown above except for ^{151}Eu , which suffers from $^{135}\text{Ba}^{16}\text{O}$ -interference.

^{45}Sc , ^{141}Pr , ^{159}Tb , ^{165}Ho and ^{169}Tm are the elements, which are mono-isotopic (100%). Pr shows no interference and Ho and Tm show negligible interference contribution from SmO and EuO, respectively. ^{159}Tb shows major interference from ^{143}NdO , and the contribution depends on the Nd/Tb concentration ratio in sample [1]. For the other elements the following analytical isotopes were selected: ^{163}Dy (24.9%), ^{160}Gd (21.86%), ^{167}Er (23.0%), ^{174}Yb (31.8%), ^{175}Lu (97.4%), ^{232}Th (100%) and ^{238}U (99.3%).

The instrument detection limits (IDLs) were calculated as the concentration equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank

(1% HNO₃) signal at the selected REEs analytical masses [12]. The method detection limits (MDLs) for the determination of dissolved analytes (REEs, Y, Th, and U) were determined using the blank solution fortified with the analytes at concentrations between two and five times the estimated IDL. The resulting MDLs were 0.5 ng/L for the REEs, Y and Th and 3 ng/L for U.

Accuracy of the method was evaluated by analysis of Spectra Pure Standards (SPS-SW1 Batch 116-Norway) for the rare earth elements (REEs), Sc, Y, Th, and U (Figure 1). Recovery percentage of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Tm, Yb, Lu, Y, Th and U varied between 95 and 107%. For Sc and Dy no good results were obtained. Potential interferences as BO₂, CaH, SiO, CO₂, and AlO can occur on ⁴⁵Sc determination and oxides as SmO and NdO may interfere on ¹⁶³Dy.

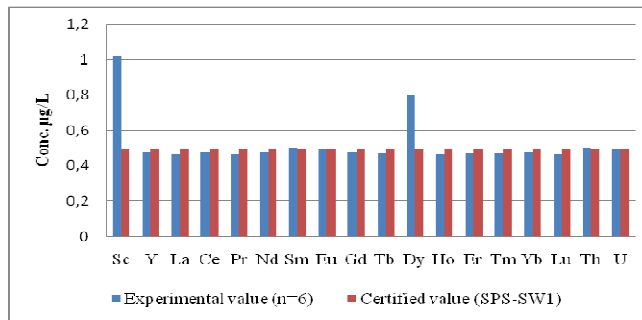


Figure 1- Methodology accuracy

3.1 Application of the ICP-MS Analytical Methodology: Spring Water Samples

The method was applied to the analysis of spring water samples collected in fountains spread throughout the historical towns of Ouro Preto, Mariana, Sabará and Diamantina in the state of Minas Gerais, Brazil. In the past these fountains played an essential and strategic role in supplying these towns with potable water. Until today this water is used by both the local population and tourists who believe in its quality. The results are shown in Figure 2.

REEs were quantified at levels comparable to those found in estuarine waters, which are characterized by low REE concentrations. The concentrations obtained range from µg to low-ng/L (ppb to ppt). As we can see in Fig. 2 the fountains from Sabará and Diamantina the concentration of REEs in the water presented the highest levels and thus possible health risks for humans may not be excluded.

As observed by earlier workers [14,15], the REEs of even atomic number (Ce, Nd, Sm, Gd, Dy, Er Yb) are more abundant than those of odd atomic number (La, Pr, Eu, Tb, Ho). It was also verified that the concentrations of light rare-earth elements (LREE) (La, Ce, Pr, Nd and Sm) are greater than those of heavy rare earth elements (HREE) (Gd, Tb, Dy, Ho, Er and Yb) in all samples. According to Markert [15] and Angelica and Da Costa [16] this fact is a typical pattern presented by plants and soils and the REEs enrichment in soils and plants may be attributed to the parent material, mainly granitic rocks. Then it may be concluded that this pattern observed in spring water samples may also be attributed to the parent material.

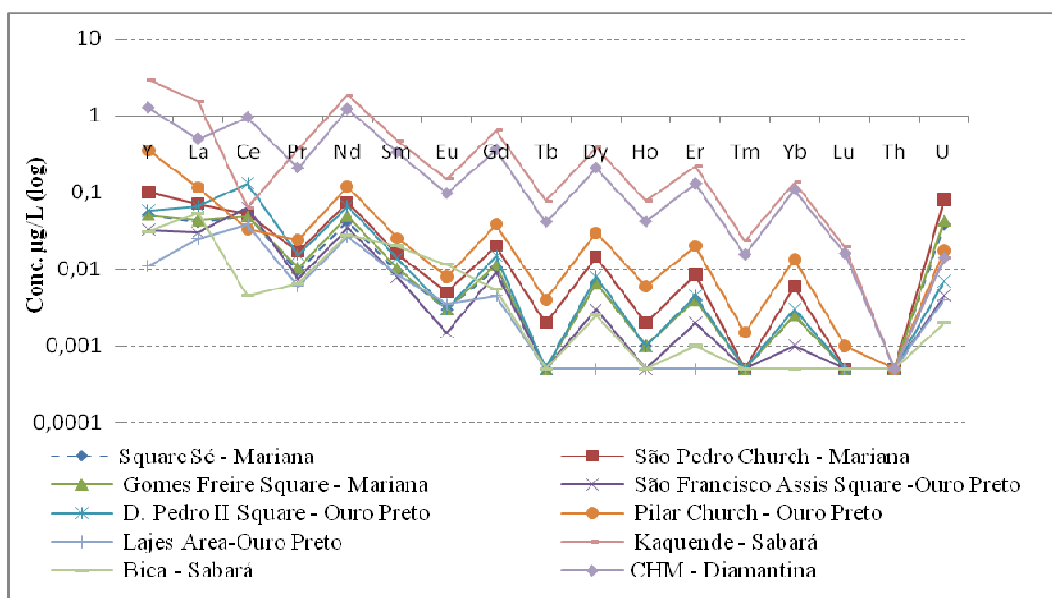


Figure 2- Results of rare earth elements, Y, Th and U in spring water samples

3. CONCLUSIONS

It has been demonstrated that ICP-QMS with external calibration and Rh as an internal standard for some elements is a rapid and accurate method for determination of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Tm, Yb, Lu, Y, Th and U in natural water with concentrations range from μg to low- ng/L (ppb to ppt). The good recovery values found for these elements in the reference material proved the accuracy of direct determination using the methodology evaluated here. The REEs patterns of the water samples reflected underlying water-rock interactions.

ACKNOWLEDGMENTS

We thank FAPEMIG (Fundação de Amparo à Pesquisa do Estado de Minas Gerais) for providing the financial support for the maintenance of the ICP-MS equipment during elaboration of this work.

REFERENCES

1. Raut, N. M., Huang, Li-Shing; Lin, King-Chuen; Aggarwal, S.K., "Uncertainty propagation through correction methodology for the determination of rare earth elements by quadrupole based inductively coupled plasma mass spectrometry", *Analytica Chimica Acta*, **530**, pp.91-103 (2005).
2. Nakamura, Y. Tsumura, Y.; Tonaogai, Y.; Shibata, T.; Ito, Y.; "Differences in behaviour among the chorides of seven rare earth elements administered intravenously to rats" *Fundamental and Applied Toxicology*", **37**, pp.106-116 (1997).

3. Prohaska, T.; Hann, S.; Latkoczy, C.; Stingeder, G.; "Determination of rare earth elements U and Th in environmental samples by inductively coupled plasma double focusing sector field mass spectrometry (ICP-SMS)" *J. Anal. At. Spectrom.*, **14**, pp.1-8 (1999).
4. Goldberg, E. D.; Koide, M.; Schmitt, R. A.; Smith, R. H.; "Rare-earth distribution in the marine environment" *J. Geophys. Res.* **68**, pp. 4209-4217.
5. Taylor, H.E.; Huff, R. A.; Montaser, A.; Novel applications of ICP-MS. In: Montaser, A. (ed.), *Inductively Coupled Mass Spectrometry*. Wiley-VCH, New York, pp. 681-807 (1998).
6. Balaram, V., "Recent trends in the instrumental analysis of rare earth elements in geological and industrial materials. *Trends Anal. Chem.* 15, pp. 475-486 (1996).
7. Dams, R. F. J.; Goossens, J. and Moens, L. "Spectral and non-spectral interferences in Inductively Coupled Plasma Mass-Spectrometry", *Mikrochim. Acta*, **119**, pp. 277 (1995).
8. Himri, M.; Pastor, A.; Guardia, M., "Determination of uranium in tap water by ICP-MS", *Fresenius J. Anal. Chem.*, **367**, pp. 151-156 (2000).
9. WHO, World Health Organization. Guidelines for drinking-water quality, addendum to vol.1, recommendations. Geneva, Switzerland: WHO (1998).
10. ATSDR. U.S. agency for toxic substances and disease registry toxicological profile for Uranium, September 1999.
11. Labrot, F.; Narbonne J. F.; Ville, P.; Saint-Denis, M.; Ribera, D.; *Archiv. Cont. Toxicological* **39**, pp. 167 (1999).
12. Wolf, R. E.; Denoyer, E., Grosser, Z.; "U.S. EPA Method 200.8 for the Analysis of Drinking Waters", Application Note D-6527, PerkinElmer Instruments, pp. 1-14 (2001).
13. Longerich, B. J.; Fryer, D. F.; Strong, D. F.; Kantipuly, C. J.; "Effects of operating conditions on the determination of the rare earth elements by inductively coupled mass spectrometry (ICP-MS)", *Spectrochim. Acta –Part B* 42, pp. 75-92 (1987).
14. Raju K. K., Raju A. N., "Biogeochemical investigation in south eastern Andhra Pradesh: The distribution of rare earths, thorium and uranium in plants and soils", *Environ. Geology*, **39** (10), pp. 1102-1106 (2000).
15. Markert, B., "The pattern of distribution of lanthanide elements in soils and plants", *Phytochemistry* **26**, pp. 3167-3170 (1987).
16. Angelica R. L., Da Costa M. L., "Geochemistry of rare-earth elements in surface lateritic rocks and soils from the Maicuru complex, Pará, Brazil", *J. Geochem. Explor.* **47**, pp. 165-182 (1993).